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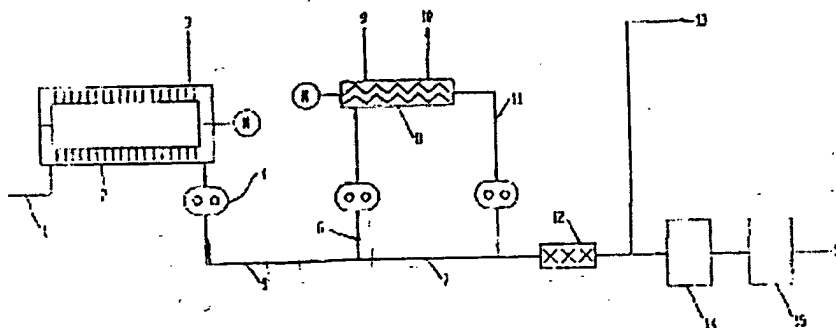
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(54) Method for Production of Polyesters with a Reduced Content of Free Acetaldehyde

(57) The invention relates to a method for the production of polyesters with a reduced content of free acetaldehyde from terephthalic acid and ethylene glycol via catalyzed polycondensation in the melt, as well as the use of this method. The method is based on the use

of highly active polycondensation catalysts, deactivation of these catalysts by addition of phosphorus-containing inhibitors and addition of substances that bind acetaldehyde. The entire polycondensation is then run at temperatures below 280°C.



Description

[0001] The invention concerns a method for production of polyesters with reduced content of free acetaldehyde from terephthalic acid and ethylene glycol via a catalyzed melt polycondensation, as well as use of this method.

[0002] Polyesters from dicarboxylic acids and diols, especially those of the polyethylene terephthalate type and its copolyesters with other dicarboxylic acids and alkylene glycols, as well as higher polycarboxylic acids and polyols, are used to a significant extent to produce containers and bottles for foods and beverages.

[0003] The plant capacities for production of such polyester granulate types have consequently risen enormously. Polyesters can be produced with large installations more cost effectively than previously. Competition of manufacturers creates price pressures. On the other hand, this stimulates the development of new application possibilities and supplants other materials, like PVC. Polyester packaging has therefore become a mass product, from whose production and sale only limited margins can be achieved. Under these circumstances any improvement or simplification of the production process that increases the margin is of interest to manufacturers of polyester packaging.

[0004] One such simplification of the production process consists of producing polyester with an average molecular weight necessary for packaging purposes, measured via the intrinsic solution viscosity (IV), by melt polycondensation. The intrinsic viscosity is then measured according to A. Horbach in phenyl/dichlorobenzene (1:1) at 25°C (C. A. Horbach, R. Binsack, H. Muller, *Angew. Makromol. Chem.* **98**(1981):35-48). The solid state final polycondensation step, now necessary without exception, thus drops out. This step is connected with significant equipment and energy expenditure: the polyester melt is initially converted to an amorphous granulate. This granulate must be reheated and worked up by crystallization in at least two stages precisely controlled in terms of temperature and residence time for subsequent solid state polycondensation (SSP). Without this demanding preparation, caking or agglomeration of the granulate occurs in SSP, which means production interruption, maintenance work and product losses. The actual SSP requires residence times between about 6 and 15 hours, as well as scavenging with inert gas, which must be processed and recycled to the process after use for economic reasons. This results in large reactor dimensions, as well as an entire series of additional equipment and units for gas scrubbing and processing with corresponding energy demands.

[0005] The space requirement and building height must be emphasized in particular. There are additional costs for solid feed, metering, and withdrawal as well as for the fact that SSP and gas processing must be conducted under high temperature and the exclusion of atmospheric oxygen.

[0006] These significant equipment and energy costs drops out if polycondensation is run to the required molecular weight in the melt. The mentioned molecular weights are the number-average weights M_n , which are determined from the IV according to Horbach et al. (see above literature source). According to the prior art, a molecular weight increase starting from about 6000 g/mol to about 20,000 g/mol has thus far been possible in the final stage of melt polycondensation. An extension to higher molecular weights of 25,000 g/mol to 35,000 g/mol, maximum 40,000 g/mol, has thus far not been considered for two reasons:

1. No final reactors were available with which higher molecular weights from 25,000 g/mol to 35,000 g/mol, maximum 40,000 g/mol, could be achieved and which could still furnish acceptable product quality measured with respect to color, free acetaldehyde and content of vinyl ester terminal groups (a gauge of thermal damage and the potential of new formation of acetaldehyde during further processing, for example, for bottles).

2. Only SSP was capable of producing a polyester granulate that had the low concentration of free acetaldehyde (AA) necessary for processing to beverage bottles and had limited AA new formation during processing of the granulate to bottles (injection molding, stretch blowing).

[0007] The development of "Discage" final reactors from the Inventa Fischer Co. has since progressed to the point that the first reason no longer plays a decisive role. Reference is made here to EP 0 719 582 and the reactor type described there with all its configuration variants is included in this application.

[0008] It is therefore possible to keep the color, AA and concentration of vinyl ester terminal groups at a level that makes the use of AA-binding additives acceptable. It has also become possible to achieve the required molecular weight increase with a single final reactor. By using two final reactors connected in succession, the molecular weight increase could certainly be reached more easily, but one would have to tolerate the drawback of longer residence time in the melt (and therefore increased formation of color, AA and vinyl ester groups), as well as the higher equipment cost.

[0009] Polyesters are produced according to the prior art by melt polycondensation from low molecular esters of dicarboxylic acids with alkylene diols [sic: alkylene glycols] at elevated temperatures during splitting off of water and alkanediols. Splitting off of the volatile products of polycondensation is driven by application of vacuum and intense agitation of the melt. Polycondensation is accelerated by addition of special catalysts, especially metal compounds,

like antimony trioxide, and achievement of higher molecular weights is made possible, as required for production of these containers.

[0010] The higher temperatures during production and processing of the melt are responsible for the decomposition reactions of the polyesters, which lead to liberation of acetaldehyde over several steps, which remains in the melt and gradually escapes from it after processing to containers and bottles, diffuses into the packaged foods and beverages and adversely affects their odor and taste.

[0011] Thermal degradation of polyesters and therefore formation of acetaldehyde, however, is also favored by the known polycondensation catalysts. They all have limited selectivity, i.e., they catalyze not only a molecular weight increase (chain extension), but (to different degrees) also molecular weight degradation by thermal ester cleavage.

[0012] The route used almost exclusively thus far for production includes polycondensation of the raw materials terephthalic acid and ethylene glycol (with addition of small amounts of comonomers, like isophthalic acid, diethylene glycol or cyclohexamethylenediol to improve the processing properties in the melt up to an average molecular weight of about 20,000 g/mol (IV 0.63)). Solid state final polycondensation is now used exclusively for a further increase in average molecular weight to values between 25,000 and 30,000, max. 40,000 g/mol, necessary for packaging purposes.

[0013] For this purpose the polyester melt, after reaching an average molecular weight of about 20,000, which is still not sufficient for production of bottles, is converted to a solid granulate. This granulate is then further condensed in a solid state polycondensation at temperatures below the melting point until the required average molecular weight is reached.

[0014] Solid state polycondensation offers the advantage that the aforementioned degradation reactions do not occur or only occur to a sharply limited degree at the lower temperatures and that acetaldehyde already present, escapes from the granulate particles under the conditions of solid state polycondensation, and is eliminated. A high molecular polyester granulate with an acetaldehyde content below 3 ppm and even less than 1 ppm is obtained in this manner, which is used for further processing into containers and bottles. Further processing of the high molecular polyester granulate essentially freed of acetaldehyde occurs according to the present state of the art in that the granulate after drying to a residual moisture content of less than 50 ppm is melted and molded to so-called blanks, which are then blown in a subsequent working step to bottles. During melting of the granulate, however, thermal loading of the material occurs again in the melt channels to the injection molds, which leads to liberation of acetaldehyde again and causes the mentioned adverse effects on the products.

[0015] Running of solid state polycondensation is also technically demanding and requires long residence times in the reaction.

[0016] Direct production, i.e., without running solid state polycondensation of high molecular polyester granules with a low content of acetaldehyde, from the polyester melt is known from US Patent 5,656,719, according to which the polyester melt is freed of acetaldehyde by introducing an inert gas to the melt and then degassing. The shortcoming here is that degassing of the polyester melt imposes high requirements on the equipment and cannot be accomplished during industrial employment of this method.

[0017] Another approach to a solution is taught in US 4,836,115 by addition of a polyamide to the polyesters. Addition of polyamides, however, has the drawback that these are immiscible with the polyesters and lead to turbidity of the polyester, so that the clarity and transparency of the product of processing (for example, a bottle) is severely compromised. At the same time, thermal degradation of polyamide leads to significant discoloration in the matrix.

[0018] A combination of these two processes, addition of polyamides and degassing of the polyester melt, is described in US 5,656,221 and US 5,258,233. Here again, however, the already mentioned drawbacks occur to the same degree.

[0019] Against this background, the task of the invention was a method for production of high molecular polyester granulate for production of containers for foods and beverages with a low content of acetaldehyde in the end product without solid state final polycondensation (SSP) as well as demanding degassing equipment.

[0020] The task is solved by a generic method with the features of Claim 1. Dependent claims 2 to 29 offer advantageous modifications of the method.

[0021] Use of the method according to the invention is characterized by the characterizing features of Claims 30 to 32.

[0022] This task is solved by a method in which the melt is polycondensed to a molecular weight sufficient for production of these products. Melt polycondensation is then run under conditions in which particularly little acetaldehyde is produced. This includes the use of highly active catalysts in a low dose and their deactivation with inhibitors as soon as the required molecular weight of the polyester, which is determined via the intrinsic viscosity (IV), is reached. In the event that the residual concentration of acetaldehyde in the blank attainable with these measures is still too high, substances are added to the melt after the required molecular weight is reached that enter into a chemical or physical bond with the acetaldehyde this is present and that is forming during processing so that the adverse effect on odor and taste is suppressed. Polycondensation is then kept at temperatures below 280°C.

[0023] The background of these expedients is as follows:

a) Use of a highly active catalyst in low concentration:

The polycondensation catalyst influences the temperature and residence time necessary to achieve the desired molecular weight. On the other hand, in addition to polycondensation, it also unavoidably catalyzes thermal degradation. These relations are generally used in industrial polycondensation processes in order to produce heat-stable polyesters. High activity of the catalyst at comparatively low temperatures of the reacting melt is assigned particular significance here. The antimony catalyst thus far used exclusively in industrial production is a compromise between reactivity and selectivity. Highly active catalysts, like titanium (IV) compounds, permit a better compromise with reference to molecular weight increase and thermal degradation by selecting a lower dose and lower reaction temperature.

b) Inhibition of the polycondensation catalyst after the desired molecular weight is reached:

During melt polycondensation, it matters that the catalyst is not inhibited by the added stabilizers. However, as soon as the desired molecular weight is reached, its task is fulfilled and its subsequent activity consists merely of catalysis of undesired reactions, like thermal ester cleavage and production of acetaldehyde and vinyl ester groups. A feature of the present invention is to reduce further production of thermal degradation products by the catalyst and thus produce a more heat-stable polyester. This occurs in that, in addition to the additive that binds acetaldehyde, a stabilizer relative to thermal degradation is added after the desired molecular weight of the melt is reached, for example, a titanium(IV) catalyst can be inhibited by the addition of a phosphorus-containing stabilizer. All phosphorus compounds are suitable as stabilizers, as long as they are soluble in the polyester melt or enter into reaction with it at the high melt viscosity, which leads to a homogeneous phase.

By means of this subsequent stabilization, it is possible, by adding an excess, not only to deactivate the titanium catalyst, but also all the trace heavy metals that enter the polyester as contaminants with the raw material or originate from abrasive or corrosive processes in the polycondensation unit. In determining the amount of added stabilizer, its inhibiting effect on the catalyst need no longer be taken into account, as is the case during addition of the stabilizer before or during polycondensation.

c) Addition of a substance that binds acetaldehyde:

In order to set a particularly low concentration of acetaldehyde in the blank, as is required, for example, to produce mineral water bottles, addition of acetaldehyde-binding substances is prescribed.

The acetaldehyde-binding additive is added in a concentration that binds not only the free acetaldehyde already present at the feed site in the polyester, but rather, it is introduced in a certain excess in relation to the free acetaldehyde concentration.

This excess binds the acetaldehyde that still forms in the melt after granulation following the feed site. In addition, it must bind newly formed acetaldehyde during remelting and injection molding so that less than 10 ppm, preferably less than 5 ppm, is present in the blank.

[0024] It is clear from this presentation that the more additives - that bind acetaldehyde - must be added, the higher the content of free acetaldehyde and vinyl ester groups (the precursor from which free acetaldehyde can form again) is in the polyester melt at the feed site. The additives according to the invention, referred to their weight, are significantly more expensive than the polyester to which they are added. In addition, they also have adverse effects on the polyester. In particular, depending on the type of compounds, these effects include weaker or stronger yellowing of the product. The invention therefore includes the least possible thermal damage to the polyester during polycondensation and up to granulation. Another object of the invention is that feed of the additives that bind acetaldehyde after polycondensation occurs in the melt. Immediately after polycondensation, the concentration of free acetaldehyde in the melt is between 1 and 10 ppm and therefore very low owing to the vacuum prevailing in the reactor. It has turned out to be ineffective to add the additive that binds acetaldehyde to the melt before the final reactor. In this case, amounts that lie well above 1% must be added and are therefore not tolerable either economically or in terms of product quality.

[0025] Turbidity in the end product could be prevented by selecting the composition and molecular weight of the acetaldehyde-binding amides, so that the refractive index of the amide is equal to that of the polyester.

[0026] The source of free and bound acetaldehyde is thermal degradation of the polyester. Technically this is an ester cleavage favored by high temperatures and long residence times. It is known in antimony-catalyzed polyesters that the activation energy of thermal degradation at about 190 kJ/mol is significantly higher than that of polycondensation (55 kJ/mol). Each degree of temperature reduction during polycondensation will therefore reduce thermal degradation much more significantly than the polycondensation rate. However, limits are imposed on the temperature reduction, because the viscosity of the melt increases with diminishing temperature. High viscosity causes stronger thermal degradation in stagnating melt regions (absence of agitation), especially in the vicinity of fixed walls. Overlapping of the positive and negative

effects leads to a temperature optimum that depends on the design of the polycondensation reactor, in addition to the catalyst. The final reactors of the "Discage" design have proven to be particularly suitable for maintaining an adequate polycondensation rate with limited thermal degradation even at melt temperatures as low as 270°C.

[0027] The mentioned expedients to reduce acetaldehyde content make it possible to limit the required amount of this additive to a concentration below 1 wt%. This is necessary for economic reasons and because the substances also have adverse side effects on the product (color, loss of molecular weight of the polyester).

[0028] Polycondensation is preferably run at a temperature below 275°C.

[0029] Addition of the inhibitor preferably occurs, when the intrinsic viscosity (IV) of the polyester melt is between 0.73 and 0.92.

[0030] An additional dicarboxylic acid, like isophthalic acid or adipic acid, is preferably added to the terephthalic acid in a concentration up to 10 mol%.

[0031] It is preferred to add additional alkanediols and/or polyols at a concentration of up to 5 mol%, in addition to ethylene glycol.

[0032] A particularly low dose of titanium catalyst below 0.1 mmol/mol dicarboxylic acid has turned out to be preferable for the thus far unpracticed production of polyesters in the melt with molecular weights to 40,000 g/mol with a minimum of thermal degradation (or minimum acetaldehyde and vinyl ester terminal group concentration), so that a particularly heat-stable polyester can be produced. The additional use of cobalt, as taught in EP 0 827 518 for production of precursor polymers with an average molecular weight to about 20,000 g/mol, to counterbalance the inhibiting effect of the phosphorus-containing stabilizers is not necessary here. At most, it is preferable to choose the concentration of titanium-containing catalyst at less than 0.05 mmol/mol dicarboxylic acid. In polycondensation experiments, it surprisingly turns out that 0.02 mmol/mol titanium/dicarboxylic acid still has the same catalytic effect at 270°C as 0.3 mmol/mol antimony.

[0033] Titanium-containing catalysts, in particular organic titanium(IV) compounds, are preferred as catalysts.

[0034] It has proven advantageous to use a phosphorus compound as inhibitor, especially an organophosphorus compound. These include many esters of phosphoric acid and phosphorous acid, as well as phosphonic and phosphonous acid. Phosphorus compounds that do not leave behind any unpleasant or even hazardous cleavage products in the polyester and whose cleavage products during further processing readily escape from the granulate or melt are preferred. In addition, they should not cause any chain degradation and therefore loss of molecular weight when mixed into the melt.

[0035] Triethyl or trimethyl phosphate are particularly suitable in this respect.

[0036] Appropriate forms of addition are as a liquid or powdered solid in pure form or mixed with the acetaldehyde-binding additive.

[0037] A concentration of organophosphorus compound of at least 1 mol/mol titanium compound is preferably chosen. Mixing of such limited amounts of phosphorus stabilizers has thus far not been practicable for industrial polyester production owing to the demanding mixing and homogenization process in the highly viscous melt. This mixing process, however, in the process according to the invention can be combined with addition of the acetaldehyde-binding additives so that this entails no additional expense.

[0038] It was surprisingly found that polyesters consisting of terephthalic acid and ethylene glycol and containing up to 5 mol% other dicarboxylic acids, like isophthalic acid, adipic acid and/or other alkanediols, like butylene glycol, hexanediol and having a free acetaldehyde content up to 100 ppm have a free acetaldehyde content of less than 10 ppm, preferably less than 5 ppm after intense mixing and conversion with a monomeric or low molecular compound from a polycarboxylic acid and the diamine of an aliphatic or aromatic hydrocarbon.

[0039] Amides from polycarboxylic acids with polybasic amines containing at least two free amino groups have proven themselves in particular for addition of acetaldehyde-binding substances. Amides consisting of dicarboxylic acids and diamines of a hydrocarbon and preferably having a molecular weight below 2000 g/mol are chosen with particular preference. It was found that these amides, if added in limited amounts to about 1 wt% to a polyester melt, lead to better transparency and clarity of the products produced with them in contrast to polyamides according to the prior art.

[0040] Appropriate amides can be produced by condensation reaction from the dicarboxylic acids and diamines mentioned in Table 1.

[0041] Another appropriate amide can be prepared by mixing an organic diamine, for example 1,3-bis(aminomethyl)benzene with the polyester melt at a temperature between 265 and 290°C in a weight ratio of 1:20 to 1:200. The reaction product can be cooled and granulated and a polyester melt with a molecular weight between 20,000 and 40,000 added to the granulate after drying as acetaldehyde-binding additive. The reaction product, however, can also be directly mixed in the molten phase with additional polyester melt of the same or different origin in order to produce products with reduced AA.

[0042] The acetaldehyde-binding additives according to the invention produce weaker or stronger yellowing of the polyester and of the bottles, containers or films produced from it. A neutral or slightly bluish tint can be imparted to the end product by the preferred addition of blue and red dyes soluble in the melt in very low concentration to the polyester melt. The yellow streak caused by the acetaldehyde-binding additives according to the invention can be compensated by this or a desired color tint can be set.

[0043] Dyes from the group of anthraquinones, for example, from the Estofil series S, especially the types Estofil blue S-RLS and Estofil red S-FBL, are suitable as dyes. Concentrations below 5 ppm, preferably below 2 ppm, have proven to be sufficient to produce a neutral or slightly bluish color tint. These dyes can be added as a strongly dilute suspension in ethylene glycol during the polycondensation process, preferably after conclusion of esterification or transesterification.

[0044] The production of a granulate with much lower crystallinity is made possible by means of the method according to the invention. Whereas granulate originating from solid state final condensation has a crystallinity of 50-60%, measured via the granulate density, the granulate according to the method of the invention has a crystalline fraction of only about 40%. To achieve complete melting in the plasticizing screw of an injection molding machine lower temperatures can be used than in granulate from solid state final polycondensation. This has an effect in the form of lower acetaldehyde new formation.

[0045] The method according to the invention offers a way to feed polyester melts directly into an injection molding machine without intermediate granulation and crystallization and to process them to blanks, as was described in DE 195 05 680. With the method according to the invention, the extruder used there can then be dispensed with. This entails a significant cost advantage, since these extruders are cost-intensive and can only be designed to limited capacities.

[0046] Intensive agitation of the acetaldehyde blocker and the inhibitor for the catalyst with the polyester melt has proven significant. A twin-screw extruder to which the polyester melt is added and in whose input region the additive is metered either in liquid form (molten) or solid form (as a granulate or powder with an average particle size less than 0.1 mm) is suitable for this. The twin-screw extruder has a degassing zone in which low molecular cleavage products of the chemical reaction between the additives and the polyester are separated by an applied vacuum by evaporation from the melt. In the case of the additive that reduces acetaldehyde, this is mostly water, which would lead to lesser or greater hydrolytic degradation of the polyester, depending on the amount of additive, without this separation capability.

[0047] In the case of large installation output, a partial stream is preferably diverted from the melt stream and passed through a twin-screw extruder. The additives are metered into this and intensely mixed into the partial stream. After degassing, the partial stream is combined again with the main stream. This is then intensely mixed and homogenized. This can occur in a static or dynamic mixer. This system has the advantage that the costly twin-screw extruder at large installation outputs can be dimensioned not for the entire melt stream, but only for a partial stream that typically accounts for about 10% of the entire stream. The then still necessary combination with a static or dynamic mixer for mixing of the partial or main stream entails lower investment costs than a twin-screw extruder laid out for the entire stream.

[0048] The method is preferably run by running the final stage of polycondensation in a reactor with a rotor designed as a hollow cylinder equipped with perforations and on which annular disks are mounted to form a melt film and to convey the polymer melt. This reactor type is further described in EP 0 719 582.

[0049] The method is used to produce packaging for foods and beverages. Production of beverage bottles and packaging films is then preferred.

[0050] The invention is further explained below with reference to Figure 1 and the subsequent practical examples.

[0051] Polyester is produced in a continuous process by esterification of terephthalic acid (TPA) with ethylene glycol (EG). A paste of 98 mol% TPA and 2 mol% isophthalic acid (IPA) is stirred in with a 1.15-fold molar amount of ethylene glycol referred to the sum of TPA and IPA. The paste is fed to an esterification reactor in which an esterification conversion of more than 90% is reached at a pressure of 2.2 bar (absolute) at a temperature of 265°C within a residence time of 90 minutes. The reactor is connected to a rectification column in which the vapors forming during the esterification reaction are separated into water and ethylene glycol, the ethylene glycol being recycled to the reactor and the water leaving the process.

[0052] The product of the first esterification reactor goes to a second reactor, where esterification is run until the concentration of carboxyl terminal groups is less than 250 mmol/kg and the degree of polycondensation is more than 6. Tetrabutyl titanate in the form of a 1% solution in ethylene glycol is supplied and mixed in this reactor as catalyst. The amount of catalyst is 0.04 mmol/mol dicarboxylic acid. The pressure in this reactor is ambient pressure, the temperature 270°C, the residence time about 1 hour. An amount of 1.2 ppm, referred to the weight of the polyester, of a heat-stable blue anthraquinone dye soluble in polyester is additionally supplied, suspended in EG and mixed with the melt.

[0053] Subsequent precondensation occurs at a vacuum of 30 mbar, a temperature of 270°C within an additional hour. The degree of polycondensation then rises to 30 and the carboxyl terminal groups decline to about 70 mol/kg. The subsequent process steps are shown in Figure 1.

[0054] This precondensate (1) goes to the final stage of polycondensation (2) in a reactor with a horizontal basket agitator of the Discage-C design from Inventa-Fischer. The temperature of the melt rises from 270°C at the inlet gradually to 275°C at the outlet. The residence time is 120 minutes, the vacuum (3) is regulated at 0.7 mbar on average so that the melt viscosity measured on-line after the reactor with a capillary viscosimeter remains constant and the intrinsic viscosity (IV) is 0.85.

[0055] The vapors from the precondensation and polycondensation reaction are condensed in spray condensers of the Inventa-Fischer design with cooled EG and the residual gases withdrawn by suction by means of four-stage jet vacuum pumps.

[0056] The melt stream is withdrawn from the final reactor with a gear pump (4) and divided into two partial streams (6) and (7), optionally after passing through a melt filter with a continuous screen changer. Division occurs so that 10% of the total stream (5) is passed through a twin-screw extruder (8). 5% terephthalic acid di(4-aminomethylbenzylamide) in molten form is added (9) to the polyester melt and intensely mixed in the twin-screw extruder. At the same time, but at a different feed site, triethyl phosphate (liquid) in pure form is added to the melt in the twin-screw extruder, in which the amount is 0.06 mmol/mol of dicarboxylic acid. Low-molecular cleavage products that form by chemical reaction of the added substances with the polyester melt are eliminated from the melt by means of vacuum through a degassing connector (10). After leaving the extruder, this melt stream (11) is combined with the main stream (7). The combined stream is homogenized in a static mixer of the Kenics type (12) and fed to a granulation device (14). The residence time of the melt between the discharge pump of the finisher and the granulation device is limited to less than 20 minutes by appropriate dimensioning of the lines. The granulate has a content of free AA of 3 ppm, measured with headspace gas chromatography.

[0057] The amorphous granulate goes to a continuous crystallizer (15), for example, described in EP 0 5 975 155, with an average residence time of 20 minutes, where it is heated during intense agitation to 170°C and converted to the semicrystalline state. After cooling to below 60°C, the granulate (16) is ready for packaging, storage or transport.

[0058] The melt present after the static mixer can also be fed directly (13) to parallel-operated injection molding machines via a melt distribution system and processed to bottle blanks.

[0059] To produce blanks for beverage bottles, the granulate is fed to a continuous polyester dryer, for example, of the Inventa-Fischer design. In the moving bed, which is traversed in countercurrent with dried air of 160°C and a dew point of -30°C, the granulate is heated to this temperature and dried to less than 50 ppm residual moisture content within a transit time of 5 hours. The dry granulate flows from the plasticizing screw to an injection molding machine, where it is processed to a melt at 275°C. The melt is forced batchwise from the machine into a cooled mold with 96 cavities through a channel system. After brief cooling the mold is opened and the finished blanks ejected. The cycle time of the process is 15 seconds. The acetaldehyde content in the wall of the blank averages 5 ppm, measured by headspace gas chromatography on the ground and homogenized blank.

Example 1

[0060] 990 g polyethylene terephthalate granulate consisting of 99 mol% terephthalic acid, 1 mol% isophthalic acid and ethylene glycol, with an intrinsic viscosity IV = 0.8 and having a content of 40 ppm free acetaldehyde is mixed with 10 g terephthalic acid di(4-aminomethyl-

benzylamide) and melted in a twin-shaft extruder at a temperature of 270-280°C, mixed into the melt, extruded into an extrudate and regranulated. The granulate contains 0.5 ppm free acetaldehyde.

Example 2

[0061] 900 g polyethylene terephthalate is mixed, as in example 1, with 100 g terephthalic acid di(4-aminomethylbenzylamide) in an extruder and extruded to an extrudate and granulated.

Example 3

[0062] 900 g PET is mixed,, as in example 1, with 100 g PET granulate produced according to example 2 and melted in an extruder, mixed, extruded and regranulated. The granulate contains 1.0 ppm free acetaldehyde.

Example 4

[0063] 990 g PET granulate is mixed as in example 1 with 10 g adipic acid di(4-aminomethylbenzylamide) and melted, mixed, extruded and regranulated in an extruder, as in example 1. The granulate contains 0.6 ppm free acetaldehyde.

Example 5

[0064] A melt stream is obtained from the finisher in a continuous installation for production of polyethylene terephthalate, in which the PET has an average molecular weight of 30,000 g/mol and a content of free acetaldehyde of 45 ppm. The melt stream is divided, so that 1/10 of the total stream is diverted and passed through a twin-screw extruder. The PET melt is mixed in the extruder with 10% terephthalic acid di(4-aminomethylbenzylamide). The melt streams 1 and 2 are then recombined, mixed in a static mixer and fed to a granulation device. The granulate has a content of free acetaldehyde of 1.5 ppm.

[0065] The granulate is dried to 50 ppm residual moisture content and melted in an injection molding machine and molded to blanks. The acetaldehyde content in the wall of the blank averages 4 ppm.

Table 1.

Dicarboxylic acid components	Diamine components
Terephthalic acid	1,3-bis(aminomethyl)benzene
Terephthalic acid and adipic acid	Hexamethylenediamine
Terephthalic acid and adipic acid	Hexamethylenediamine and 1,3-bis(aminomethyl)benzene

Claims

1. Method for production of polyesters with reduced free acetaldehyde content from terephthalic acid and ethylene glycol via catalyzed melt polycondensation, in which
 - a) the catalyst is added before polycondensation,
 - b) after an intrinsic viscosity (IV) of the melt between 0.63 and 1.00 is reached, which is reached without solid state final polycondensation, an inhibitor is added for deactivation of the catalyst and
 - c) an excess of the substance that binds the free acetaldehyde is then added, so that subsequently liberated acetaldehyde is also bound,in which, during the entire polycondensation process, a temperature below 280°C is maintained.
2. Method according to Claim 1, characterized by the fact that polycondensation is run at a temperature below 275°C.
3. Method according to at least one of the preceding Claims, characterized by the fact that the inhibitor added in step b) has an intrinsic viscosity (IV) between 0.73 and 0.92.
4. Method according to at least one of the preceding Claims, characterized by the fact that an additional dicarboxylic acid, like isophthalic acid or adipic acid, is added in a concentration of 10 mol%, in addition to terephthalic acid.

5. Method according to at least one of the preceding Claims, characterized by the fact that additional alkanediols and/or polyols are added in a concentration up to 5 mol%, in addition to ethylene glycol.
6. Method according to at least one of the preceding Claims, characterized by the fact that the concentration of catalyst in step a) is less than 0.1 mmol/mol dicarboxylic acid.
7. Method according to at least one of the preceding Claims, characterized by the fact that the concentration of catalyst in step a) is less than 0.05 mmol/mol dicarboxylic acid.
8. Method according to at least one of the preceding Claims, characterized by the fact that a titanium-containing catalyst is used in step a).
9. Method according to at least one of the preceding Claims, characterized by the fact that an organic Ti(IV) compound is used in step a).
10. Method according to at least one of the preceding Claims, characterized by the fact that a phosphorus-containing inhibitor is used in step b).
11. Method according to at least one of the preceding Claims, characterized by the fact that an organophosphorus compound is used in step b).
12. Method according to at least one of the preceding Claims, characterized by the fact that trimethyl or triethyl phosphate is used in step b).
13. Method according to at least one of the preceding Claims, characterized by the fact that the concentration of organophosphorus compound is at least 1 mol/mol titanium in step b).
14. Method according to at least one of the preceding Claims, characterized by the fact that the organophosphorus compound is mixed together with the acetaldehyde-binding additive into the melt.
15. Method according to at least one of the preceding Claims, characterized by the fact that the amide from a polycarboxylic acid and a polybasic amine containing at least two free amine functions is used in step c).

16. Method according to at least one of the preceding Claims, characterized by the fact that the amide of a dicarboxylic acid and a diamine is used in step c).
17. Method according to at least one of the preceding Claims, characterized by the fact that the amide has an average molecular weight below 2000 in step c).
18. Method according to at least one of the preceding Claims, characterized by the fact that the amide is used in a concentration of less than 1 wt% in step c).
19. Method according to at least one of the preceding Claims, characterized by the fact that terephthalic acid and/or adipic acid is used in step c) as dicarboxylic acid and hexamethylenediamine and/or 1,3-bis(aminomethyl)benzene is used as diamine.
20. Method according to at least one of the preceding Claims, characterized by the fact that terephthalic acid is used in step c) as dicarboxylic acid and 1,3-bis(aminomethyl)benzene as diamine.
21. Method according to at least one of the preceding Claims, characterized by the fact that only a diamine, like hexamethylenediamine or 1,3-bis(aminomethyl)benzene, is added in step c), which forms amides with the dicarboxylic acids present in the polyester melt.
22. Method according to at least one of the preceding Claims, characterized by the fact that, during or after polycondensation, a dye soluble in polyester is added to correct the color of the end product.
23. Method according to at least one of the preceding Claims, characterized by the fact that, during or after polycondensation, dyes from the anthraquinone group are added.
24. Method according to at least one of the preceding Claims, characterized by the fact that the dye is added in a concentration below 5 ppm.
25. Method according to at least one of the preceding Claims, characterized by the fact that the polyester melt after polycondensation and mixing of all additives is granulated and the amorphous granulate is crystallized.

26. Method according to at least one of the preceding Claims, characterized by the fact that the crystalline fraction of the granulate is less than 40% measured via the density.
27. Method according to at least one of the preceding Claims, characterized by the fact that the polyester melt after polycondensation and after mixing of the additives is fed directly to an injection molding machine for production of blanks.
28. Method according to at least one of the preceding Claims, characterized by the fact that, in steps b) and c), a partial stream of the melt is diverted from a melt stream originating from a continuous polycondensation, into which the additives are metered in an extruder with degassing capability and mixed, in which the low-molecular degradation products are eliminated from the melt by a vacuum and the partial stream is then recombined with the main stream of melt and mixed intensely.
29. Method according to at least one of the preceding Claims, characterized by the fact that the final stage of polycondensation is run in a reactor with a rotor designed as a hollow cylinder provided with perforations and on which annular disks are fastened to form a melt film and to convey the polyester melt.
30. Use of the method according to at least one of the preceding Claims to produce packaging for foods and beverages.
31. Use of the method according to at least one of the Claims 1 to 29 to produce beverage bottles
32. Use of the method according to at least one of the Claims 1 to 29 to produce packaging film.

